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著者	渡辺　和雄
journal or publication title	IEEE Transactions on Applied Superconductivity
volume	11
number	1
page range	3892-3895
year	2001
URL	http://hdl.handle.net/10097/47137

doi: 10.1109/77.919918

Field Dependence of J_c for Filamentary RE-Ba-Cu-O Superconductors Prepared by a Solution Spinning Method

Tomoko Goto and Kazuo Watanabe

***Abstract*—The filamentary RE-Ba-Cu-O (RE = Nd, Nd-Eu-Gd, and Nd-Sm-Eu-Gd) precursor was prepared by a solution spinning method, through a homogeneous aqueous solution containing mixed acetates of RE, Ba and Cu, poly(vinyl alcohol) and organic acids. The filamentary precursor was partially melted in flowing 0.1%O_2+Ar or 1%O_2+Ar and then oxygenated under various conditions. The transport critical current density (J_c) of the samples was measured in magnetic fields up to 10 T at 77 K. The influence of field dependence of J_c on the initial different RE elements in the filamentary RE-Ba-Cu-O superconductors was examined. The field dependence of J_c was improved by mixing three or four different RE elements. The J_c value at 77 K and up to 6 T for the sample partially melted in flowing 0.1%O_2+Ar was higher than that for the sample melted in flowing 1%O_2+Ar. The highest J_c value of more than 1.76 x10^4 A/cm^2 at 77 K and 9 T was detected for filamentary Nd-Sm-Eu-Gd-Ba-Cu-O superconductors partially melted in flowing 0.1%O_2+Ar.**

***Key words*— Field dependence of J_c, Filamentary RE-Ba-Cu-O, Oxygen controlled melt growth, Solution spinning.**

I. Introduction

The oxygen controlled melt growth (OCMG) process for RE-Ba-Cu-O (RE is Nd or compound with two, three and four rare-earth elements) superconductors is effective in achieving high transition temperature (T_c) value and high critical current density (J_c) value in a high magnetic field region accompanied by a secondary peak effect at 77 K [1]. The secondary peak effect was ascribed to the so-called ΔT_c pinning provided by RE rich 123 (RE 123ss) clusters, which were uniformly distributed in the RE123 matrix. However, the peak field and J_c values were found to be dependent on the kind of rare earth elements and on the processing condition [2]. Recently, enhancement of J_c by 211 particles in ternary $Nd_{0.33}Eu_{0.33}Gd_{0.33}Ba_2Cu_3Ox$ melt-processed superconductors was also reported [3].

Fabrication of RE-Ba-Cu-O superconductors in the form of tapes or wires with high J_c value in high magnetic fields at 77K is necessary for practical applications of superconducting magnets and power transmission lines.

We have studied preparation of filamentary RE-Ba-Cu-O superconductors with high J_c value by a solution spinning method and the OCMG process [4]. We observed different J_c-$\mu_0 H$ curves for the filamentary RE-Ba-Cu-O superconductors as the heating conditions and initial precursor compositions were changed [5]-[7]. In this paper, the influence of field dependence of J_c on the initial different RE elements in the filamentary RE-Ba-Cu-O superconductors was examined.

II. Experimental

The filamentary RE-Ba-Cu-O precursor was produced by dry spinning through a homogeneous aqueous solution containing mixed acetates of RE, Ba and Cu, poly(vinyl alcohol), propionic acid and 2-hydroxy isobutyric acid. An acetate mixture with a nominal composition of RE : Ba : Cu = 1.18 : 2.12 : 3.09 (RE = Nd (sample (1)), $Nd_{0.333}Eu_{0.333}Gd_{0.333}$ (sample (2)), and $Nd_{0.25}Sm_{0.25}Eu_{0.25}Gd_{0.25}$ (sample (3))) was dissolved in the solution. Then we increased the concentration of the solution to obtain a stable viscous homogeneous spinning dope. The dope was extruded as a filament into a hot air zone and coiled on a winding drum. The precursor filament was heated to 450 °C at a heating rate of 25 °C/h to remove any volatile components. Then calcination was carried out at 900 °C for 15 min in flowing oxygen in order to remove CO_2 from the sample. The calcined sample was partially melted in flowing 0.1%O_2+Ar and 1%O_2+Ar. A two-step heat treatment in flowing O_2 was employed for oxygenation of the sample. The first step of the treatment was at 500 °C for 5 h and the second step was at around 340 °C for 15 h. The diameter of the resulting filamentary sample was about 60 μm.

The transport J_c of the samples at 77 K was measured by a standard four-probe resistive method. Silver paint was used to connect the silver sputtered parts of the sample to Ag electrodes 100 μm in diameter for supplying DC currents and 75 μm in diameter for voltage leads. The sample was embedded in a substrate using phenolic resin (PR-50702K, supplied by Sumitomo Bakelite) and set on a sample holder. External magnetic fields were applied in a direction normal to the filament length using a helium-free 11 T superconducting magnet at the High Field Laboratory for

Manuscript received August 10, 2000.

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Superconducting Materials, Tohoku University. Currents were passed along the direction of the filament length. The J_c was defined by the offset method from the point on the I-V curve at which the voltage of 0.2 μV appeared between the voltage terminals separated by 2 mm.

III. Results and Discussion

A. J_c for the samples partially melted in flowing $1\%O_2$+Ar

The partial melting in flowing $1\%O_2$+Ar for the calcined samples was examined under various conditions to obtain high J_c values at 77 K and zero field. The calcined sample (1) was partially melted at 1020 °C for 30 min, cooled to 890 °C at a cooling rate of 40 °C/h, then cooled to 390 °C at a cooling rate of 50 °C/h, followed by furnace cooling in flowing $1\%O_2$+Ar. Two-step heat treatment in pure oxygen gas flow was employed for oxygenation of the sample. The calcined samples (2) and (3) were partially melted at 1010 °C for 30 min.

Temperature dependence of the electrical resistivity for the samples is shown in Fig. 1. The T_c, ΔT_c and resistivity (ρ) values at 150 K of the samples are listed in Table 1. As the number of different RE element increases, the resistivity value at 150 K decreases. A considerably lower T_c value of 88 K with wide range of transition of 5 K is observed for sample (2).

Field dependence of J_c for the sample prepared by various heating conditions was measured. Fig. 2 shows optimized J_c-μ_oH curves for the samples. A voltage fluctuation of 1 μV on the I-V curves for sample (1) was observed by applying high magnetic fields more than 6 T. The source of the fluctuation comes from the texture and structure of the sample. While sample (1) had a few voids in the step-like bulky grains, a dense and well-aligned texture was observed for samples (2) and (3). The structure of sample (1) was mixture of the orthorhombic 123 and Nd422 phases. On the other hand samples (2) and (3) had a mixed structure of orthorhombic 123 and RE 211 phases. The J_c value decreases slightly with increasing applied field. A clearly anomalous peak effect, which is often observed for the bulk OCMG processed RE-Ba-Cu-O, is not observed in the J_c-μ_oH curves for the present samples. The field dependence of J_c for the samples is improved by mixing three or four different RE elements. A high J_c value more than 6000 A/cm^2 at 77 K and 9 T is observed for sample (3). Such a high J_c value at 77 K and 9 T was not reported for the bulk OCMG processed RE-Ba-Cu-O superconductors.

The plots of pinning force F_p ($F_p = J_c \times \mu_oH$) vs. applied field (μ_oH) at 77 K for the samples partially melted in flowing $1\%O_2$+Ar are shown in Fig. 3. The pinning force increased with increasing the number of mixed different RE elements. Maximum F_p value is observed at 8 T for sample (3). On the other hand, a plateau of the F_p value at wide range of applied field is observed for samples (1) and (2), indicating overlapping of various pinning mechanisms. The flux pinning in ternary RE-Ba-Cu-O (RE = Nd-Eu-Gd)

TABLE I
THE ZERO RESISTIVITY TEMPERATURE (T_C), WIDTH OF THE TRANSITION TEMPERATURE (ΔT_C) AND NORMAL RESISTIVITY (ρ) VALUE AT 150 K FOR THE FILAMENTARY RE-Ba-Cu-O SUPERCONDUCTORS.

Sample	RE elements	Atmosphere	T_c (K)	ΔT_c (K)	ρ (mΩ·cm)
(1)	Nd	$1\%O_2$+Ar	94.5	1.5	0.37
(2)	Nd-Eu-Gd	$1\%O_2$+Ar	88	5	0.16
(3)	Nd-Sm-Eu-Gd	$1\%O_2$+Ar	95	2	0.05
(1)	Nd	$0.1\%O_2$+Ar	91	4	0.63
(2)	Nd-Eu-Gd	$0.1\%O_2$+Ar	92	3	0.10
(3)	Nd-Sm-Eu-Gd	$0.1\%O_2$+Ar	92	2	0.21

OCMG processed bulk sample was studied by M.R.Koblischka et al. [8]. It was reported that characteristic for all RE compounds was a solid solution between the RE atoms and Ba, which provided composition fluctuation throughout the sample. These composition fluctuations

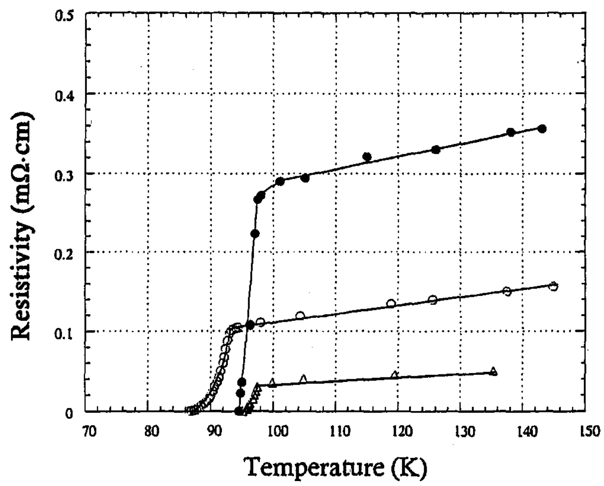

Fig. 1. Resistivity as a function of temperature for samples partially melted in flowing $1\%O_2$+Ar. • sample (1), o sample (2), Δ sample (3).

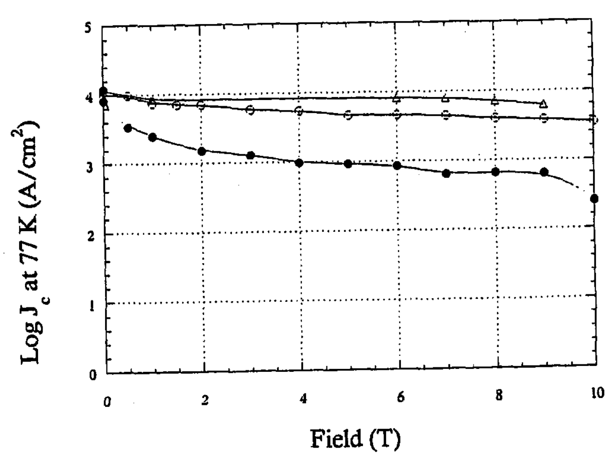

Fig. 2 J_c vs. applied field curve at 77 K for samples partially melted in flowing $1\%O_2$+Ar. • sample (1), o sample (2), Δ sample (3).

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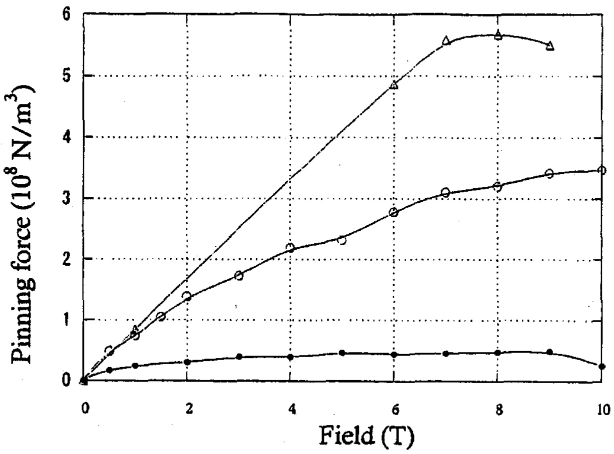

Fig. 3. Relation between pinning force and applied field at 77 K for samples partially melted in flowing $1\%O_2$+Ar.
• sample (1), o sample (2), Δ sample (3).

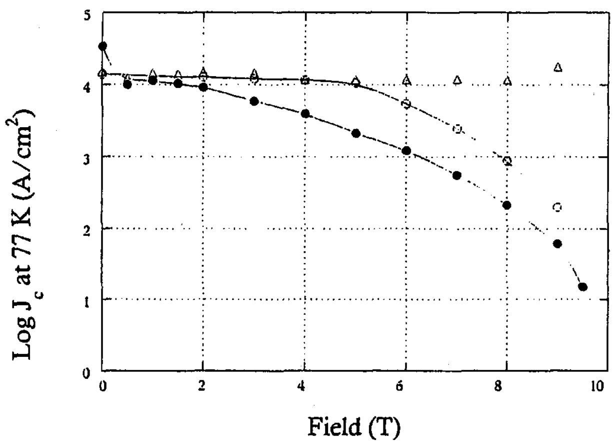

Fig. 4. J_c vs. applied field curve at 77 K for samples partially melted in flowing $0.1\%O_2$+Ar. • sample (1), o sample (2), Δ sample (3).

resulted in spatial variations of the T_c, and increased flux pinning by means of the Δκ or ΔT_c pinning mechanism. We attempted the scaling of the extended pinning force F_p/F_{pmax} (F_{pmax} denotes the maximum value of F_p) versus the reduced field H/H_{max} ($\mu_o H_{max}$ is the field at F_{pmax}) for sample (3). The plots were fitted to the curve based on ΔT_c pinning mechanism [9].

B. J_c for the samples partially melted in flowing $0.1\%O_2$+Ar

The calcined sample (1) was partially melted at 990 °C for 10 min, cooled to 910 °C at a cooling rate of 30 °C/h, followed by furnace cooing in flowing $0.1\%O_2$+Ar. Samples (2) and (3) were partially melted at 980 °C for 10 min in flowing $0.1\%O_2$+Ar. A two-step treatment was employed for oxygenation of the sample. Temperature dependence of the resistivity for the samples was measured. The T_c, ΔT_c and ρ values at 150 K are summarized in Table 1. T_c values around 92 K with ΔT_c of about 3 K are measured for these samples. The ρ value of sample (1) is 3-6 times higher than that for samples (2) and (3).

The J_c of the samples prepared by various heating conditions was measured in magnetic fields up to 10 T at 77 K. The optimized field dependences of J_c for the samples are shown in Fig. 4. An accurate measurement of the J_c value for sample (3) was not performed due to sample burnout. However, high J_c value of more than 1.76 x10^4 A/cm^2 was maintained by applying field of 9 T at 77 K. Applying magnetic fields more than 6 T resulted in a voltage fluctuation of 1 μV on the I-V curves for sample (1). The field dependence of J_c is improved by increasing the mixed number of different RE elements. A clearly anomalous peak effect is not observed in the J_c-$\mu_o H$ curves for these samples. However, a plateau of the J_c value at the wide range of field is observed and the width of the plateau increased with increasing the mixed number of different RE elements. The J_c value of around 10^4 A/cm^2 is maintained up to 2 T and 5 T for samples (1) and (2) and more than 9 T for sample (3), respectively. The J_c values at 77 K and up to 6 T for the samples partially melted in flowing $0.1\%O_2$+Ar are higher than those for the samples partially melted in flowing $1\%O_2$+Ar.

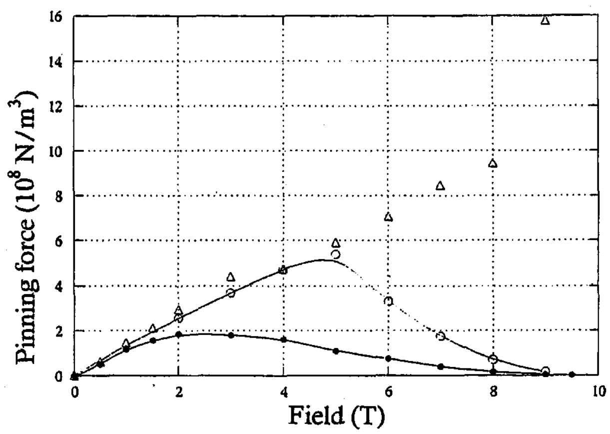

Fig. 5. Relation between pinning force and applied field at 77 K for samples partially melted in flowing $0.1\%O_2$+Ar.
• sample (1), o sample (2), Δ sample (3).

Fig. 5 shows the relation between pinning force F_p versus applied field for the samples partially melted in flowing $0.1\%O_2$+Ar. The pinning force also increases with increasing the mixed number of the different RE elements. Maximum F_p value was observed at 5 T for sample (2) and broad peak at 2 T for sample (1). The pinning force for the samples partially melted in flowing $0.1\%O_2$+Ar is higher than that for the samples partially melted in flowing $1\%O_2$+Ar.

Unlike Y123, which forms only a stoichiometric compound, the light rare earth elements form a solid solution of Re rich 123. It was reported that the lower limit of solid solubility for Nd123 was a function of both temperature and oxygen partial pressure (PO_2). For Sm123, Eu123 and Gd123, the upper limit of solid solubility was a function of PO_2 [10].

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There are significant compositional regions for various RE 123ss, where by changing PO_2 it is possible to move from a homogeneous solid solution to a multiphase mixture. High T_c phase of RE 123ss can be stabilized in low PO_2. On the other hand, change of the solid solubility limits offers a practical way to introduce defects as flux pinning center [10]. It is considered that these RE 123ss in the present filamentary samples play an important role for the flux pinning force.

A fracture surface and a polished and etched surface of sample (3) are shown in Fig. 6. Dense and well-aligned texture is observed. The RE compositional fluctuation in the present filamentary RE-Ba-Cu-O sample results in denser texture with preferred orientation of the grains.

Thus the properties for sample (1) are considerably different from samples (2) and (3). This comes from the texture and structure of the sample. It is considered that a temperature range for the liquidus phase during the partial melting became to be wider, and dense and well-aligned texture was obtained by mixing RE elements. Moreover, mixing different RE element reduced the weak link behavior. On the other hand, it should be noted that the present filamentary sample starts from chemical-liquid phase and may contain a microscopic feature such as fine chemical contamination or oxygen defect and twin plane as well as compositional fluctuations of RE 123ss. Therefore the pinning mechanism for the present filamentary sample turns to be quite complex and various defects are introduced as flux pinning center.

IV. Conclusion

The effect of initial different RE elements for the filamentary RE-Ba-Cu-O superconductors on the field dependence of J_c at 77 K was examined. The field dependence of J_c was improved by increasing the mixed number of the different RE elements. The J_c value at 77 K and up to 6 T for samples partially melted in flowing $0.1\%O_2$+Ar was higher than that for the samples partially melted in flowing $1\%O_2$+Ar. The highest J_c value of more than 1.76×10^4 A/cm^2 at 77 K and 9 T was achieved for the filamentary (Nd-Sm-Eu-Gd)-Ba-Cu-O superconductors partially melted in flowing $0.1\%O_2$+Ar and oxygenation. The pinning force for the sample partially melted in flowing $0.1\%O_2$+Ar was higher than that for the sample in flowing $1\%O_2$+Ar. The pinning force increased with increasing the mixed number of the different RE elements.

Acknowledgment

We thank M. Takahama, T. Kimura, K. Inagaki, F. Takeuchi and K. Iwata for their assistance in experimental work.

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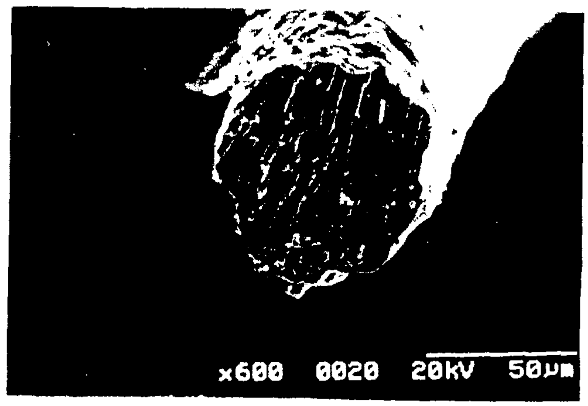

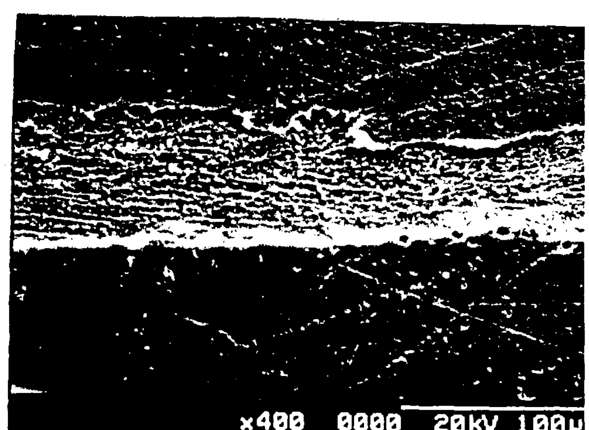

Fig. 6. Fracture surface and polished etched surface on the longitudinal cross-section of sample (3) partially melted in flowing $0.1\%O_2$+Ar.

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